

The effect of the support composition on the hydrodesulfurization activity and selectivity in MoS₂ catalysts

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Introduction

Since the 1970's, the US federal government has enacted regulations aimed at producing cleaner burning fuels with the goal of reducing air pollution. Federal regulations have resulted in the introduction of lead-free gasoline, lower evaporative emissions, addition of oxygenates during winter months, and significantly lower levels of sulfur in diesel fuels. While these changes have improved air quality, the US petroleum refining industry faces further regulatory pressure to decrease the level of sulfur in transportation fuels.

Sulfur in gasoline diminishes the efficiency of an automobile's catalytic converter, resulting in increased NO_x and hydrocarbon emissions. The US national average contains about 350 ppm S, while nearly one-fourth of the gasoline contains over 500 ppm S. Although the 1990 Clean Air Act Amendments led to significant reductions in auto exhaust emissions, the Environmental Protection Agency (EPA) is now considering whether more stringent emission standards will be required in order to achieve the nation's air quality goals. The EPA is proposing to lower the sulfur level in gasoline in the 22 states with the lowest air quality to 150 ppm. In addition, in states where air pollution is minimal, sulfur in gasoline will be reduced to about 300 ppm. Future regulations could possibly restrict S in gasoline to less than 100 ppm.

In this study, MoS₂ catalysts with and without Co on different supports have been evaluated for hydrodesulfurization and olefin hydrogenation of FCC naphtha. The MoS₂ particle size of these catalysts has been determined by x-ray absorption fine structure (XAFS) and x-ray diffraction (XRD), and used to estimate the turnover rate (TOR). The results of catalysts testing indicate that while the support has a small effect on the TOR of the catalysts, the support has no effect on the olefin hydrogenation selectivity.

Methods and Materials

The XAFS measurements were made at the Materials Research Collaborative Access Team (MR-CAT) insertion device beamline. Measurements were made in transmission mode with ionization chambers optimized for maximum current with linear response ($\sim 10^{10}$ photons detected/sec). A double-crystal Si(111) monochromator with resolution of better than 4 eV at 20 keV (Mo-K edge) was used along with a Pt-coated mirror to minimize the presence of harmonics.

The sample environment was an *in situ* cell, which allowed us to pre-treat samples off line prior to XAFS analysis. Approximately 0.5 g of presulfided catalyst were pressed between polished steel dies into a self-supporting wafer inside a cylindrical, steel sample holder. The sample thickness was chosen to give an absorption edge step, $\Delta\mu x$, of ~ 1.0 . The sample was placed in the center of the 45 cm x 2 cm cylindrical sample cell. This cell was fitted with Kapton windows at both ends and a flow-through gas system. Prior to the XAFS measurements, the presulfided catalysts were heated to 350° C for one hour at atmospheric pressure in a flow of 5% H₂ in He. The sample cell was cooled and purged with He gas. The data were then collected at room temperature under a static He atmosphere. Related studies of supported MoS₂ catalysts have shown that they are relatively insensitive to oxygen at room temperature. Therefore, the low permeability of the window to oxygen over the duration of these measurements did not affect the results.

Standard procedures were used to extract the $\chi(k)$ data from the absorption spectra using *winxas97* software [1]. Phase shifts and backscattering amplitudes were obtained from reference compounds (Na₂MoO₄·H₂O for Mo-O, and MoS₂ for Mo-S and Mo-Mo). Experimental reference spectra were also compared with theoretically calculated spectra from *feff* (version 7.0) [2]. The data were fit in *r*-space (and *k*-space) from $\Delta r = 1.10\text{--}3.35 \text{ \AA}$ ($\Delta k = 2.90\text{--}13.90 \text{ \AA}^{-1}$, with k^2 weighting).

Results

Qualitative evaluation of the XAFS data as well as detailed fitting reveals that all of the catalysts are in the MoS₂ phase [3]. Within the limits of the statistical accuracy of the fits, in all samples the Mo is coordinated to S at a distance of 2.41 Å, and Mo at a distance of 3.16 Å, but with an increased Debye-Waller factor. The reduced amplitude of the Mo-S and Mo-Mo paths indicates that the MoS₂ particles are small on all of the catalysts. As the amplitude of the Mo-Mo peak decreases, there is a corresponding, but not proportional, decrease in the amplitude of the Mo-S peak (See Figure 1).

XRD measurements were made on these catalysts to determine the particle size and to identify the phases present. In two samples, no diffraction peaks due to the MoS₂ were visible, indicating a very small particle size. In the others, the diffraction peaks due to the support interfered with the peaks due to the in-plane ordering, and an analysis of the particle size anisotropy was not possible.

Analysis of the coordination number and calibrating to a theoretical model of the coordination number vs. particle size allowed a semirigorous quantification of the size of the catalyst particles present [4]. These results compared favorably to the sizes measured with XRD in those cases where a comparison was possible. In all of the catalysts, except for MoS₂ on silica-alumina, the particle sizes were the same within 30%, at about 20 Å.

There was no apparent effect of the support composition the olefin selectivity, which was linear with sulfur conversion. The addition of Co, however, had a large effect on the olefin selectivity. Up to a conversion of 85%, there was relatively low olefin-hydrogenation conversion, at which point conversion increased rapidly.

Acknowledgments

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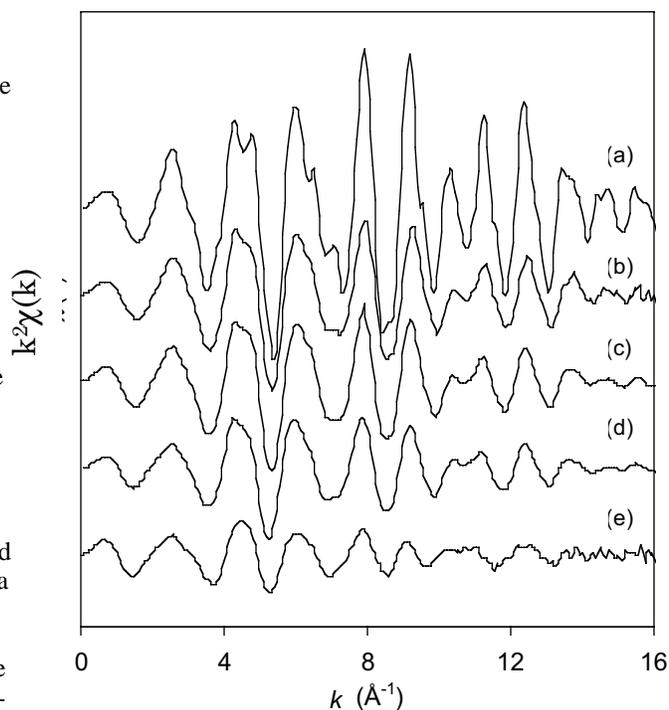


Figure 1: Isolated Mo K-edge XAFS for MoS₂ on various supports in order of decreasing Mo layer size: (a) bulk powder - unsupported, (b) SiO₂, (c) Al₂O₃-2%Cs, (d) Al₂O₃, (e) SiO₂-Al₂O₃.